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(54) Title: ISOCYANATE-CROSSLINKED COATINGS HAVING REDUCED YELLOWING

(57) Abstract

This invention relates to a clear or colorless coating that is free of yellow discoloration, and a method for the production thereof, utilizing a pyrazole compound as a blocking agent for the blocked polyisocyanate employed in the coating composition. Also disclosed is a coated article comprising a painted or unpainted substrate having a coating provided using the above-described coating composition.

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ISOCYANATE-CROSSLINKED COATINGS HAVING REDUCED YELLOWING

This invention relates generally to clear or colorless coatings made using blocked polyisocyanates and, more specifically, to clear coatings that are free of yellow discoloration.

Frequently used commercial methods for producing clearcoats for automotive and other coatings applications involve application of a clearcoat composition over a high-solids basecoat. Clearcoat compositions can be characterized as being of the one-component type or the two-component type. In the two-component or "two-pack" system, the polymer and the cross-linking agent are combined just prior to coating. However, this two-component process generally requires mixing of the components in the right proportion immediately prior to coating, and is expensive to operate and difficult to control. In contrast, the one-component or "one-pack" systems offer significant advantages in manufacturability because the cross-linkable clearcoat coating composition can be coated as one formulation. However, when highly reactive crosslinking agents such as polyisocyanates are used, the cross-linking agent in one-component systems must be blocked in order to prevent premature cross-linking of the clearcoat composition. The blocking group can then be unblocked under specified conditions, such as an elevated temperature, to allow the materials to crosslink so the coating can be cured.

Up until recently, an elevated temperature of 160°C or more was required to cause unbl cking of the polyisocyanate in order to enable the desired

clear-coat to form during the coating operation. Recently, there has been a trend in the industry to discover blocking agents that unblock at lower temperatures, thereby affording an energy savings during production of the desired coating, regardless of whether a clear-coat or a pigmented paint is desired. Illustrative examples of blocking agents that provide unblocking at lower temperatures are the pyrazole-containing compounds as disclosed in U.S. Patent No. 4,976,837 for use in pigmented paint compositions.

Clearcoats that have been cross-linked with blocked isocyanate cross-linking agents also exhibit good hardness, and they are also resistant to environmental etch, i.e., etch appearing as milky or cloudy marks on clearcoat finishes that have been exposed to the elements. Unfortunately, however, these clearcoats suffer from severe yellowing during heat curing. Moreover, unlike coatings derived from unblocked aromatic polyisocyanates, coatings derived from blocked isocyanates tend to exhibit significant yellowing during cure even when an aliphatic polyisocyanate is used.

Heretofore, attempts to reduce the yellow discoloration of clearcoats that have been cross-linked with blocked isocyanates have typically utilized additives to inhibit or otherwise minimize the yellow discoloration problem. By way of illustration, U.S. Patent No. 5,216,078 discloses the addition of a hydrazide group, either attached to the blocked polyisocyanate itself, or attached to the polyisocyanate-reactive polymer (e.g., polyol) in the formulation, or attached to another compound

as a formulation additive. Unfortunately, the introduction of extraneous hydrazide moieties to the clearcoat-forming formulation can adversely affect the formulation and/or processing expense of the resulting clearcoat.

In view of the above, new methodology for providing a one-component polyisocyanate-cross-linked clear coating which avoids discoloration without the use of discoloration-prevention additives would be highly desired by the clear coatings manufacturing community.

In one aspect, the present invention relates to a method of producing a clear polyurethane coating on a substrate which comprises coating the substrate with a pigment-free coating composition consisting essentially of a polyisocyanate blocked with a pyrazole compound blocking agent and an isocyanate-reactive polymer, said coating composition being free of hydrazide moieties (and preferably free of other yellow discoloration prevention additives).

In another aspect, the present invention relates to a method of using a pyrazole compound blocked isocyanate to provide a clear coating on a substrate which is free of yellow discoloration, said method comprising coating a painted or unpainted substrate (advantageously a metal or plastic substrate) with a pigment-free coating composition consisting essentially of a polyisocyanate blocked with a pyrazole compound blocking agent and an isocyanate-reactive polymer, said coating composition being free of hydrazide moieties (and preferably free of other yellow discoloration prevention additives).

In yet another aspect, the present invention relates to a method of using a pyrazole compound-blocked polyisocyanate in order to provide a clear coating on a substrate which comprises the steps of:

(a) forming a pigment-free coating composition comprising a mixture of said pyrazole compound blocked polyisocyanate and a polymer containing at least one isocyanate-reactive functional group, said coating composition being free of hydrazide compounds, and

(b) contacting said pigment-free coating composition with a substrate in order to form a clear coating on said substrate.

In still another aspect, the present invention relates to a coated article comprising a painted or unpainted substrate and a coating on said substrate free of yellow discoloration and formed by:

(a) forming a pigment free coating composition comprising a mixture of said pyrazole compound blocked polyisocyanate and a polymer containing at least one isocyanate-reactive functional group, said coating composition being free of hydrazide compounds, and

(b) contacting said pigment-free coating composition with a substrate in order to form a clear coating on said substrate.

These and other aspects of the present invention will become readily apparent upon reading the following detailed description of the invention.

It has now been surprisingly found in accordance with the present invention that the

yellow discoloration problem associated with clearcoats that have been cross-linked using blocked isocyanates is suitably avoided and/or minimized by using a pyrazole compound as a blocking agent. Without wishing to be bound by any particular theory, it is believed that the clear, colorless property associated with the coatings of the present invention is attributable, at least in part, to a combination of the relatively low unblocking temperature of the pyrazole blocking agent and the color stability of the blocking agent and the after unblocking in the coating formulation.

The composition according to the present invention comprises a polymer having at least one functional group that is reactive with isocyanate. Such polymers include, for example, acrylic polymers, modified acrylic polymers, polyesters, polyepoxides, polycarbonates, polyurethanes, polyamides, polyimides, and polysiloxanes, all of which are well-known in the art. Preferably, the polymer is an acrylic, modified acrylic or polyester. More preferably, the polymer is an acrylic polymer. The above polymers may have any of a number of known functional groups that are reactive with isocyanate. Such groups include, for example, hydroxyl groups, amino groups, and thiol groups.

In one preferred embodiment of the invention, the polymer is an acrylic. Such polymers are well-known in the art, and can be prepared from monomers such as methyl acrylate, acrylic acid, methacrylic acid, methyl methacrylate, butyl methacrylate, cyclohexyl methacrylate, and the like.

The functional group that is reactive with isocyanate, e.g., hydroxyl, can be incorporated into the ester portion of the acrylic monomer. For example, hydroxy-functional acrylic monomers that can be used to form such polymers include hydroxyethyl acrylate, hydroxybutyl acrylate, hydroxybutyl mcthacrylatc, hydroxypropyl acrylate, and the like. Aminofunctional acrylic monomers would include t-butylaminoethyl methacrylate and t-butylaminoethylacrylate. Other acrylic monomers having isocyanate reactive functional groups in the ester portion of the monomer are also within the skill of the art.

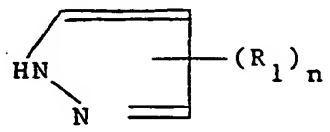
Modified acrylics can also be used as the polymer (a) according to the invention. Such acrylics are typical]y polyester-modified acrylics or polyurethane-modified acrylics, as is well-known in the art. An example of one preferred polyester-modified acrylic is an acrylic polymer modified with alpha-caprolactone. Such a polyester modified acrylic is described in U.S. Pat. No. 4,546,046 of Etzell et al. Polyurethane-modified acrylics are also well-known in the art. They are described, for example, in U.S. Pat. No. 4,584,354.

Polyesters having hydroxyl groups, acid groups, or amino groups as isocyanate-reactive groups can also be used as the polymer in the composition according to the invention. Such polyesters are well-known in the art, and may be prepared by the polyesterification of organic polycarboxylic acids (e.g., phthalic acid, hexahydrophthalic acid, adipic acid, maleic acid) or their anhydrides with organic polyols containing primary or secondary hydroxyl

groups (e.g., ethylene glycol, butylene glycol, neopentyl glycol).

The composition according to the present invention utilizes a blocked isocyanate as a curing agent for the above-described polymers. Compounds suitable as the isocyanate portion of the blocked isocyanate are well known in the art, and include toluene diisocyanates, isocyanurates of toluene diisocyanate, diphenylmethane 4,4'-diisocyanate, isocyanurates of 4,4'-diisocyanate, methylenebis-4,4'-isocyanatocyclohexane, isophorone diisocyanate ("IPDI"), isocyanurates of isophorone diisocyanate ("IPDI trimer"), IPDI biuret, 1,6-hexamethylene diisocyanate ("HDI"), isocyanurates of 1,6 hexamethylene diisocyanate ("HDI trimer"), HDI biuret, 1,4-cyclohexane diisocyanate, p-phenylene diisocyanate, and triphenylmethane 4,4',4"-triisocyanate, tetramethyl xylene diisocyanate, metaxylene diisocyanate, and polyisocyanate oligomers and other adducts. The preferred polyisocyanates are HDI trimer, HDI biuret, IPDI trimer, IPDI biuret, and combinations thereof.

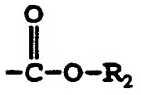
The blocking agents used in the present invention are pyrazoles of the formula:



where R_1 and n are as defined as follows:

n is is 0, 1, 2 or 3

wherein R_1 is, or, where n is more than 1, each R_1, which may be the same or different, is a C_1-C_4 alkyl, C_1-C_4 alkenyl, phenyl C_1-C_4 alkyl, phenyl, NO_2-,≤ halogen or



group. Examples of the pyrazoles described include 3,5-dimethylpyrazole, 4-nitro-3,5-dimethylpyrazole, 4-benzyl-3,5-dimethylpyrazole, methyl 5-methylpyrazole-3-carboxylate, 4-bromo-3,5-dimethylpyrazole, pyrazole, 3-methyl-5-phenyl-pyrazole and 3,5-dimethylpyrazole-4-carboxanilide (prepared by condensation of hydrazine acetate with diacetoacetanilide).

The blocked isocyanate is preferably present in the coating composition in an amount of from about 10 weight percent to about 60 weight percent, and more preferably from about 15 weight percent to about 40 weight percent.

A solvent may optionally be utilized in the one-component clearcoat formulation used in the present invention. Although the formulation of the present invention may be utilized, for example, in the form of substantially solid powder, or a dispersion, it is often desirable that the formulation used in the present invention is in a substantially liquid state, which can be accomplished with the use of a solvent. This solvent should act as a solvent with respect to both the hydroxy-functional polymer as well as the

blocked isoyanate. Preferably the solvent is present in an amount effective to substantially solubilize both the hydroxy-functional polymer and the blocked isocyanate. In general, the solvent can be any organic solvent and/or water. Preferably, the solvent is a polar solvent, as polar solvents may allow the blocking agent to dissociate (i.e. deblock) at lower temperatures. More preferably, the solvent is a polar aliphatic solvent or polar aromatic solvent. Still more preferably, the solvent is a ketone, ester, acetate, aprotic amide, aprotic sulfoxide, aprotic amine, and water. Examples of useful solvents include methyl ethyl ketone, methyl isobutyl ketone, m-amyl acetate, ethylene glycol butyl ether-acetate, propylene glycol monomethyl ether acetate, xylene, n-methylpyrrolidone, and blends of aromatic hydrocarbons.

The solvent may be present in the coating composition in an amount of from about 0.01 weight percent to about 99 weight percent, preferably from about 10 weight percent to about 60 weight percent, and more preferably from about 30 weight percent to about 50 weight percent.

The catalyst may be present in the coating composition in an amount of from about 0.01 weight percent to about 10 weight percent, preferably from about 0.1 weight percent to about 2 weight percent, and more preferably about 0.5 weight percent. The above-described coating compositions can be coated on the article by any of a number of techniques well-known in the art. These include, for example, spray coating, dip coating, roll coating, curtain

coating, and the like. For automotive body panels, spray coating is preferred.

In one preferred embodiment, the clear and/or colorless coating composition according to the invention is used over a pigmented basecoat as part of a composite color-plus-clear coating. Such composite coatings are popular for their depth of color and liquid glossy surface appearance. They have found particularly wide acceptance in the field of automotive coatings.

Pigmented basecoat compositions for such composite coatings are well-known in the art, and do not require explanation in detail herein. Polymers known in the art to be useful in basecoat compositions include acrylics, vinyls, polyurethanes, polycarbonates, polyesters, alkyds, and polysiloxanes. Preferred polymers include acrylics and polyurethanes. Basecoat polymers are preferably crosslinkable, and thus comprise one or more type of cross-linkable functional groups. Such groups include, for examplc, hydroxy, isocyanate, amine, epoxy, acrylate, vinyl, silane, and acetoacetate groups. These groups may be masked or blocked in such a way so that they are unblocked and avaiable for the crosslinking reaction under the desired curing conditions, generally elevated temperatures. Useful cross-linkable functional groups include hydroxy, epoxy, acid, anhydride, silane, and acetoacetate groups. Preferred cross-linkable functional groups include hydroxy functional groups and amino functional groups.

Basecoat polymers may be self-cross-linkable, or may require a separate cr ss-linking agent that

is reactive with the functional groups of the polymer. When the polymer comprises hydroxy functional groups, for example, the cross-linking agent may be an aminoplast resin, isocyanate and blocked isocyanates (including isocyanurates), and acid or anhydride functional crosslinking agents.

After the article is coated with the above-described layers according to the invention, the coated article is subjected to conditions so as to cure the coating layers. Although various methods of curing may be used, heatcuring is preferred. Generally, heat curing is effected by composing the coated article to elevated temperatures provided primarily by radiative heat sources. Curing temperatures will vary depending on the particular blocking groups used in the cross-linking agents, however they generally range between 120°C. and 175°C., and are preferably between 132°C. and 157°C. The invention is particularly effective at reducing yellowing that takes place when cure temperatures exceed 141°C., and especially when cure temperatures exceed 163°C. The curing time will vary depending on the blocking agents, and physical parameters such as the thickness of the layers, however, typical curing times range from 15 to 60 minutes.

The invention is further described in the following example.

Example 1

HEAT AGING AND UV AGING COMPARISON OF CLEAR COATINGS PRODUCED USING A DMP BLOCKING AGENT VERSUS A MEKO BLOCKING AGENT

(A) Heat Aging

In order to determine the coating color stability associated with the use of a pyrazole blocking agent DMP, as compared with a commercial blocking agent, methylethylketoxine ("MEKO") the following evaluation was made.

Coating formulations were prepared utilizing an acrylic polyol (100 pbw of G-CURE 105P70, a product of Henkel Corporation having a hydroxyl equivalent weight of 516 on a solids basis "acrylic polymer #1" or 100 pbw of "acrylic polymer #2" from Korea Chemical company having a hydroxyl equivalent weight of 467 on a solids basis), a flow aid (0.68 pbw of a 10% solution of FC 430 a product of 3M Company), 4 pbw of a 10% solution dibutyltin dilaurate catalyst, 70 pbw of a solvent blend (a 1:1:1 weight ratio blend of butyl acetate, methyl amyl ketone, and ethoxyethyl propionate) in order to provide a coating formulation spray viscosity of 20 seconds, and HDI trimer or a blend of HDI trimer with IPDI trimer. The trimer was employed in the amounts shown in Table I below. The coating formulations employed a blocked NCO/OH ratio of 1.1/1 for each formulation.

Steel test panels precoated with BONDERITE 1000 and a white acrylic-melamine basecoat were spray

coated with each of the eight coating formulations identified in Table I. The coating on each panel was allowed to room temperature dry for 5 to 15 minutes, and then the panels were oven baked at a temperature of 280°F for 20 minutes. The panels were then "overbaked" at an oven temperature of 305°F for 30 minutes in order to check for "overbake" yellowing resistance of the coating in the event of a plant malfunction leading to an excessive baking temperature and/or time period in the curing oven.

Standard coating physical property tests were performed, and the test results are provided in Table I below.

TABLE I

Formulation No.	1	2	3	4	5	6	7	8
Acrylic Polyol #1 (pbw)	100	100			100	100		
Acrylic Polyol #2 (pbw)			100	100			100	100
FC430 (10 % solution) (pbw)	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68
Dibutyl Tin Dilaurate (10 % solution) (pbw)	4	4	4	4	4	4	4	4
Sovent Blend (pbw)	70	80	70	75	70	70	70	70
HDI Trimer w/DMP (pbw)	56.43	45.14	68.59	54.87				
IPDI Trimer w/DMP (pbw)		13.34		16.21				
HDI Trimer w/MEKO (pbw)					54.00	43.20	65.64	52.51
IPDI Trimer w/ MEKO (pbw)						12.89		15.67
VOC (lbs / gal	3.33	3.53	3.30	3.39	3.77	3.77	3.81	3.81
gms / liter)	400	424	396	407	452	452	457	457
Zahn #2, seconds	20.2	18.8	20.7	20.8	20.9	20.9	21.8	21.4
Dry film Thickness, mils	4.0	3.5	3.9	4.1	4.0	4.1	4.2	4.1
20 ° Gloss	89	89	90	89	88	85	94	93
60 ° Gloss	94	94	95	94	94	92	94	93

TABLE 1 (Continued)

Formulation No.	1	2	3	4	5	6	7	8
Yellowness Index (YIE-313)								
Before Heat Age	0.39	1.22	-0.57	-0.62	7.12	8.39	5.51	5.18
After Heat Age	2.10	3.41	0.25	1.74	16.37	17.23	11.91	10.64
Impact, in-lbs								
Foward	40	35	40	40	40	35	70	60
Reverse	<5	<5	<5	<5	<5	<5	15	<5
Pencil Hardness	4	4	4	4	4	4	4	4
Conical Mandrel	Pass	Fail	Pass	Fail	Pass	Fail	Pass	Pass
Adhesion	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
MEK Double Rubs (100)	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Acid Etch Resistance** (Hours to failure 12 = best, 1 = worse)	8	9	10	11	11	12	11	12

acid etch test is a drop test using a blend of acids (65 parts 1.0 N H_2SO_4, 30 parts 1.0 HNO_3 and 5 parts 1.0 N HCl). One drop of acid is placed on the panel every hour for a total of twelve drops. The acid is washed off using water and dried overnight. The panels are visually inspected for spot damage. The longer time to spotting the better etch resistance.

The yellowness index test was conducted on each test panel before and after heat aging using the ASTM E-313 yellowness Index test in a Hunter laboratory COLORQUEST spectrophotometer. The yellowness index results demonstrate significant improvement in the color of the DMP-blocked formulations (Formulations 1-4) as compared to the MEKO-blocked formulations (Formulations 5-8) for coatings made from the HDI trimer-based and the HDI trimer/IPDI trimer based blend formulations.

(B) UV Light Aging

In another comparison, using QUV (B) light aging of the coatings made with the above HDI trimer in combination with acrylic polymer #1 (from Table I above), and without using any UV stabilizers, the DMP-blocked coating formulation provided a yellowness index after 888 hours of 14.2 as compared to an index of 44 provided using the MEKO-blocked coating formulation using the ASTM E-313 yellowness index test procedure. Thus, the DMP-blocked formulation provided a much improved, whiter coating then did the MEKO-blocked formulation after unblocking.

As used herein, the term "pbw" designates "parts by weight". Unless stated otherwise, all amounts given herein are provided on a weight basis.

While the invention has been described above with reference to specific embodiments thereof, it is apparent that many changes, modifications and variations can be made without departing from the inventive concept disclos d herein. Accordingly, it

is intended to embrace all such changes, modifications and variations that fall within the spirit and broad scope of the appended claims.

WHAT IS CLAIMED IS:

1. A method of producing a clear polyurethane coating on a substrate which comprises coating the substrate with a pigment-free coating composition characterized by consisting essentially of a polyisocyanate blocked with a pyrazole compound blocking agent and an isocyanate-reactive polymer, said coating composition being free of hydrazide moieties.

2. A method of using a pyrazole compound blocked isocyanate to provide a clear coating on a substrate which is free of yellow discoloration, said method being characterized by coating a painted or unpainted substrate with a pigment-free coating composition consisting essentially of a polyisocyanate blocked with a pyrazole compound blocking agent and an isocyanate-reactive polymer, said coating composition being free of hydrazide moieties.

3. A method of using a pyrazole compound-blocked polyisocyanate in order to provide a clear coating on a substrate which is characterized by the steps of:

(a) forming a pigment-free coating composition comprising a mixture of said pyrazole compound blocked polyisocyanate and a polymer containing at least one isocyanate-reactive functional group, said coating composition being free of hydrazide compounds, and

(b) contacting said pigment-free coating composition with said substrate in order to form said clear coating on said substrate.

4. A coated article comprising a painted or unpainted substrate and a coating on said substrate free of yellow discoloration and characterized by being formed by:

(a) forming a pigment-free coating composition comprising a mixture of said pyrazole compound blocked polyisocyanate and a polymer containing at least one isocyanate-reactive functional group, said coating composition being free of hydrazide compounds, and

(b) contacting said pigment-free coating composition with a substrate in order to form a clear coating on said substrate.

5. The method of claim 1 characterized in that said pyrazole compound is selected from the group consisting of 3,5-dimethylpyrazole, 4-nitro-3,5-dimethylpyrazole, 4-benzyl-3,5-dimethylpyrazole, methyl 5-methylpyrazole-3-carboxylate, 4-bromo-3,5-dimethylpyrazole, pyrazole, 3-methyl-5-phenyl-pyrazole and 3,5-dimethylpyrazole-4-carboxanilide (prepared by condensation of hydrazine acetate with diacetoacetanilide).

6. The method of claim 2 characterized in that said pyrazole compound is selected from the group consisting of 3,5-dimethylpyrazole, 4-nitro-3,5-dimethylpyrazole, 4-benzyl-3,5-dimethylpyrazole, methyl 5-methylpyrazole-3-carboxylate, 4-bromo-3,5-dimethylpyrazole, pyrazole, 3-methyl-5-phenyl-pyrazole and 3,5-dimethylpyrazole-4-carboxanilide (prepared by condensation of hydrazine acetate with diacetoacetanilide).

7. The method of claim 3 characterized in that said pyrazole compound is selected from the group consisting of 3,5-dimethylpyrazole, 4-nitro-3,5-dimethylpyrazole, 4-benzyl-3,5-dimethylpyrazole, methyl 5-methylpyrazole-3-carboxylate, 4-bromo-3,5-dimethylpyrazole, pyrazole, 3-methyl-5-phenyl-pyrazole and 3,5-dimethylpyrazole-4-carboxanilide (prepared by condensation of hydrazine acetate with diacetoacetanilide).

8. The coated article of claim 4 characterized in that said pyrazole compound is selected from the group consisting of 3,5-dimethylpyrazole, 4-nitro-3,5-dimethylpyrazole, 4-benzyl-3,5-dimethylpyrazole, methyl 5-methylpyrazole-3-carboxylate, 4-bromo-3,5-dimethylpyrazole, pyrazole, 3-methyl-5-phenyl-pyrazole and 3,5-dimethylpyrazole-4-carboxanilide (prepared by condensation of hydrazine acetate with diacetoacetanilide).

9. The method of claim 1 characterized in that said polyisocyanate is selected from the group consisting of 1,6-hexamethylene diisocyanate trimer, 1,6-hexamethylene biuret, isophorone diisocyanate trimer, isophorone diisocyanate biuret, and combinations thereof.

10. The method of claim 2 characterized in that said polyisocyanate is selected from the group consisting of 1,6-hexamethylene diisocyanate trimer, 1,6-hexamethylene biuret, isophorone diisocyanate trimer, isophorone diisocyanate biuret, and combinations thereof.

11. The method of claim 3 characterized in that said polyisocyanate is selected from the group consisting of 1,6-hexamethylene diisocyanate trimer, 1,6-hexamethylene biuret, isophorone diisocyanate trimer, isophorone diisocyanate biuret, and combinations thereof.

12. The coated article of claim 4 characterized in that said polyisocyanate is selected from the group consisting of 1,6-hexamethylene diisocyanate trimer, 1,6-hexamethylene biuret, isophorone diisocyanate trimer, isophorone diisocyanate biuret, and combinations thereof.

13. An improved one component coating composition for providing a clear coating on a substrate, the improvement comprising that said composition is characterized by being free of any hydrazide component and said composition consisting essentially of an isocyanate-reactive polymer and a blocked polyisocyanate having a pyrazole compound as a blocking agent.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/09212

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C08G 18/80
US CL : 528/45; 427/385.5
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 528/45; 427/385.5

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CHEMICAL ABSTRACTS: search terms: pyrazole, isocyanate, polyisocyanate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A, 4,008,247 (Tucker) 15 February 1977, see abstract, col. 1, line 37-col. 2, line 13, col. 13, lines 32-34, col. 14, lines 12-20	1-3,5-7
X	Cooray et al, "The Chemistry and Technology of Blocked Isocyanates", Paint And Resin, October 1988, pp. 18-19, see col. 1, lines 1-13 and col. 2, lines 18-21.	1-3
X	US,A, 4,623,731 (Ivanov et al) 18 November 1986, see col. 1, lines 35-38, col. 2, lines 5-19, col. 2, lines 66-67, col. 3, lines 17-25	1-3
X	EP,A, 159,117 (Baxenden Chemical Company) 23 October 1985, see abstract, col. 3, lines 17-25, col. 4, lines 8-14, col. 5, lines 9-25.	1-3,5-7,9- 11

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 17 OCTOBER 1994	Date of mailing of the international search report 22 NOV 1994
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer SHRIVE BECK Telephone No. (703) 308-2333

Form PCT/ISA/210 (second sheet)(July 1992)*

XP-002253520

1/16 - (C) WPI / DERWENT
AN - 2002-210402 [27]
AP - JP20000080856 20000322
CPY - DUPO
DC - A17 A85 A95 E13 L03 U11 U12
FS - CPI;EPI
IC - C08K5/13 ; C08K5/17 ; C08K5/3492 ; C08L23/26 ; C08L101/02
MC - A04-F06B A04-G08A A08-A01A E06-D05 E07-D05 E07-D13B E10-E02D3 L03-D05A L03-E05B
- U11-A07 U12-A02A4E
M3 - [01] B615 B701 B713 B720 B815 B831 F012 F014 F015 F016 F017 F019 F022 F163 F199 F433 F499 F580 G001 G002 G011 G012 G013 G014 G015 G016 G020 G021 G022 G029 G040 G100 G221 H401 H481 J583 M1 M113 M115 M116 M119 M126 M129 M135 M139 M148 M149 M210 M211 M240 M283 M313 M314 M320 M321 M322 M331 M332 M340 M342 M344 M372 M373 M382 M391 M392 M411 M413 M510 M522 M523 M530 M531 M540 M782 M904 M905 Q454 Q620 Q624 R043; 00212 00262 01649; 0054-57204-K 0054-57204-M
- [02] F012 F014 F016 F017 F019 F433 G010 G011 G030 G100 G563 H521 H602 H641 H714 H721 J011 J221 L472 M123 M126 M137 M141 M210 M211 M212 M213 M214 M215 M216 M220 M221 M222 M223 M224 M225 M226 M231 M232 M233 M240 M262 M272 M281 M283 M320 M413 M510 M521 M530 M531 M540 M541 M782 M904 M905 Q454 Q620 Q624 R043; 0054-57203-K 0054-57203-M
- [03] D012 D022 D810 G010 G011 G014 G015 G017 G100 H2 H211 H4 H401 H441 H541 H602 H608 H609 H641 H642 H643 H8 M111 M210 M211 M212 M213 M214 M215 M216 M220 M221 M222 M223 M224 M225 M226 M231 M232 M233 M240 M272 M280 M281 M282 M320 M412 M511 M520 M531 M532 M540 M782 M904 M905 Q454 Q620 Q623 R043; 0054-57201-K 0054-57201-M
- [04] F012 F014 F016 F580 G010 G015 G017 G018 G019 G020 G021 G029 G040 G100 G113 G221 G299 H5 H543 H8 M1 M111 M112 M113 M119 M210 M211 M212 M213 M214 M215 M216 M220 M221 M222 M223 M224 M225 M226 M231 M232 M233 M240 M272 M281 M282 M283 M320 M413 M510 M521 M533 M540 M782 M904 M905 Q454 Q620 R043; 00212; 0054-57202-K 0054-57202-M
- [05] G017 G019 G100 H4 H404 H444 H8 J0 J014 J2 J273 M210 M214 M233 M240 M283 M312 M315 M321 M323 M332 M334 M342 M344 M372 M382 M383 M391 M393 M414 M510 M520 M533 M540 M782 M904 M905 Q454 Q620 R043; R05344-K R05344-M
PA - (DUPO) MITSUI DU PONT POLYCHEMICAL KK
PN - JP2001261904 A 20010926 DW200227 C08L23/26 006pp
PR - JP20000080856 20000322
XA - C2002-064086
XIC - C08K-005/13 ; C08K-005/17 ; C08K-005/3492 ; C08L-023/26 ; C08L-101/02
XP - N2002-160809
AB - JP2001261904 NOVELTY - An ethylene copolymer resin composition (I) comprises
- (A) 100 parts by weight ethylene/(meth)acrylic acid copolymer or its ionomer ,
- (B) 0.05-5 parts UV-light absorber composed of benzotriazole(s) or triazole(s),
- (C) 0.05-5 parts lower molecular weight hindered amine light stabilizer,
- (D) 0.05-5 parts higher molecular weight hindered amine light stabilizer and

- (E) 0.01-5 parts hindered phenol antioxidant.
- USE - (I) is useful as sealant for solar cell and material for preparation of exterior trim parts (claimed).
- ADVANTAGE - (I) has good moldability, transparency, mechanical strength, light resistance and chemical resistance.
- (Dwg.0/0)

CN - 0054-57204-K 0054-57204-M 0054-57203-K 0054-57203-M 0054-57201-K 0054-57201-M 0054-57202-K 0054-57202-M R05344-K R05344-M

IW - ETHYLENE COPOLYMER RESIN COMPOSITION USEFUL LIGHT RESISTANCE MATERIAL PREPARATION EXTERIOR TRIM PART COMPRISE ETHYLENE METHO ACRYLIC ACID COPOLYMER ULTRAVIOLET LIGHT ABSORB LIGHT STABILISED ANTIOXIDANT

IKW - ETHYLENE COPOLYMER RESIN COMPOSITION USEFUL LIGHT RESISTANCE MATERIAL PREPARATION EXTERIOR TRIM PART COMPRISE ETHYLENE METHO ACRYLIC ACID COPOLYMER ULTRAVIOLET LIGHT ABSORB LIGHT STABILISED ANTIOXIDANT

NC - 001

OPD - 2000-03-22

ORD - 2001-09-26

PAW - (DUPO) MITSUI DU PONT POLYCHEMICAL KK

RRL - 00212 00262 01649

TI - Ethylene copolymer resin composition useful as e.g. light-resisting material for preparation of exterior trim parts comprises ethylene/(meth)acrylic acid copolymer, UV-light absorber, light stabilizer and antioxidant

A01 - [001] 018 ; R00326 G0044 G0033 G0022 D01 D02 D12 D10 D51 D53 D58 D82 ; R00460 G0306 G0271 G0260 G0022 D01 D12 D10 D26 D51 D53 D58 D60 D84 F36 F35 ; P0588 ; H0022 H0011 ; M9999 M2415 ; M9999 M2379-R ; P1150 ; P0088 ; P0179

- [002] 018 ; Q9999 Q8968-R ; Q9999 Q7512 ; B9999 B3623 B3554 ; B9999 B4397 B4240 ; K9847-R K9790 ; B9999 B4091-R B3838 B3747 ; B9999 B4615 B4568 K9847 ; B9999 B4580 B4568 ; ND04 ; B9999 B4728 B4568
- [003] 018 ; Gm ; H0157
- [004] 018 ; R05344 D01 D11 D10 D19 D18 D34 D50 D63 D76 D95 F33 F30 F41 F91 ; A999 A497 A486 ; A999 A771
- [005] 018 ; G2540-R D01 D22 D45 D77 F11 N- 5A ; A999 A544 A486 ; K9869 K9847 K9790 ; A999 A771
- [006] 018 ; D01 F07-R ; A999 A544 A486 ; K9869 K9847 K9790 ; A999 A771
- [007] 018 ; A999 A248-R

XP-002253521

(C) WPI / DERWENT
AN - 1998-434025 [37]
AP - JP19960343365 19961224
CPY - UBEI
DC - A23 A85 E19 X12
FS - CPI;EPI
IC - C08K5/00 ; C08L77/00 ; H01B3/30
MC - A05-F03 A08-A01B E05-G09B E07-D13C E10-B04 E10-E02U
X12-D03B1 X12-D03D X12-E02B
M3 - [01] F011 F012 F014 F016 F017 F019 F433 H1 H181 H2 H201 H4 H402 H421 H481 H8 J0 J012 J2 J272 M210 M211 M240 M272 M282 M283 M312 M322 M332 M342 M343 M372 M383 M391 M413 M510 M521 M530 M540 M782 M903 M904 Q130 Q620; 9837-EPL01-K 9837-EPL01-M
- [02] D012 D810 G017 G100 H2 H211 H4 H401 H441 H8 M210 M214 M233 M240 M282 M320 M412 M511 M520 M531 M540 M782 M903 M904 Q130 Q623; R12222-K R12222-M
- [03] B515 B713 B720 B813 B831 G015 G019 G100 M1 M121 M129 M148 M149 M210 M214 M233 M240 M283 M320 M411 M510 M520 M533 M540 M782 M903 M904 Q130; R05373-K R05373-M
- [04] G017 G019 G100 H4 H402 H442 H5 H582 H8 J0 J012 J2 J272 M210 M211 M214 M233 M240 M283 M312 M323 M332 M342 M372 M383 M392 M393 M414 M510 M520 M532 M540 M782 M903 M904 Q130; R12854-K R12854-M
PA - (UBEI) UBE IND LTD
PN - JP10182874 A 19980707 DW199837 C08K5/00 007pp
PR - JP19960343365 19961224
XA - C1998-131402
XIC - C08K-005/00 ; C08L-077/00 ; H01B-003/30 ; (C08K-005/00 C08K-005/13 C08K-005/17 C08K-005/3492 C08K-005/49)
XP - N1998-339040
AB - J10182874 PA resin compsn. consists of (A) 100 pts. wt. of PA 11 and/or PA 12, (B) 0.05-2 pts. wt. of hindered phenol-type heat stabilisers, (C) 0.05-2 pts. wt. of P-type processing stabilisers, (D) 0.05-2 pts. wt. of triazole-type UV absorbers, and (E) 0.05-2 pts. wt. of (a) low molecular- and (b) high molecul ar hindered amine-type light stabilisers. The wt. ratio of (a)/(b) is 1/10-10/1.
- USE - The resin compsn. is used as materials for cable sheaths.
- ADVANTAGE - The resin compsn. has improved colour tone stability and weather resistance for a long time.
- (Dwg.0/0)
C - C08K5/00 C08K5/13 C08K5/17 C08K5/3492 C08K5/49
CN - 9837-EPL01-K 9837-EPL01-M R12222-K R12222-M R05373-K R05373-M R12854-K R12854-M
IW - POLYAMIDE RESIN COMPOSITION COMPRISE POLYAMIDE HINDERED PHENOL HEAT STABILISED TRI AZOLE ULTRAVIOLET ABSORB HINDERED AMINE LIGHT STABILISED
IKW - POLYAMIDE RESIN COMPOSITION COMPRISE POLYAMIDE HINDERED PHENOL HEAT STABILISED TRI AZOLE ULTRAVIOLET ABSORB HINDERED AMINE LIGHT STABILISED
NC - 001
OPD - 1996-12-24
ORD - 1998-07-07
PAW - (UBEI) UBE IND LTD
TI - Amide] resin composition - comprises polyamide 1,1 or 1,2, hindered phenol heat stabilisers, tri:azole UV absorbers and hindered amine

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      light stabilisers
A01 - [001] 018 ;  P0668 P1934 P0635 F70 D01 D11 D10 D50 D91 ;
    - [002] 018 ;  P0679 P1934 P0635 F70 D01 D11 D10 D50 D92 ;
    - [003] 018 ;  ND00 ;  ND01 ;  Q9999 Q7352 Q7330 ;  B9999 B4728 B4568 ;
      B9999 B3907 B3838 B3747 ;  K9745-R ;
    - [004] 018 ;  D01 F30-R ;  A999 A511 A486 ;
    - [005] 018 ;  G2562 G2540 D01 D22 D45 D77 F11 N- 5A D33 D19 D18 D76 D11
      D10 D50 D94 F31 F30 ;  A999 A544 A486 ;  K9869 K9847 K9790 ;
    - [006] 018 ;  D01 F07-R ;  K9870 K9847 K9790 ;  A999 A544 A486 ;
    - [007] 018 ;  D01 D11 D10 D19 D18 D33 D76 D50 D95 F52 ;  A999 A486-R ;
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